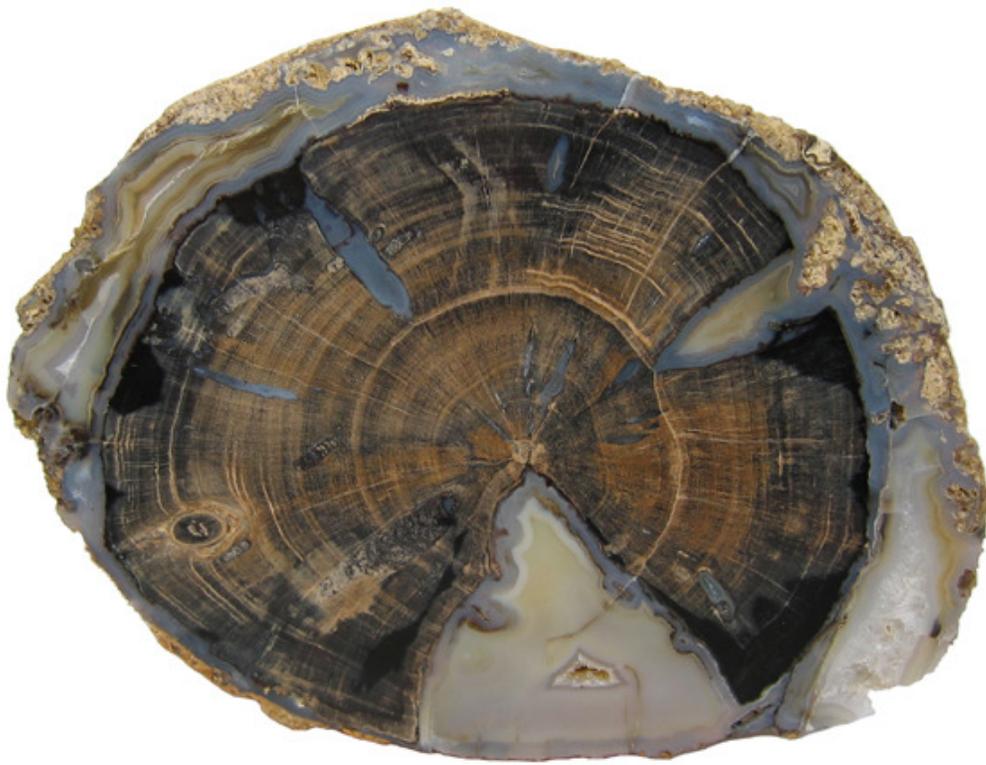


Petrified Wood:
The Silicification of Wood by Permineralization
Mike Viney



Schinoxylon sp.
Laney Shale Member, Green River Formation
Eocene
Blue Forest, Wyoming

Introduction

Organisms entombed in sediment, such as volcanic ash, which becomes saturated with water, may petrify or permineralize under the right pH and temperature conditions. Traditionally, petrification or petrification refers to animal or plant tissue that has turned to stone. Petrified wood and dinosaur bone are familiar examples; however, these fossils actually form through permineralization and often contain original organic material. In this article we will use petrification and permineralization synonymously.

Permineralized fossils form when solutions rich in minerals permeate porous tissue, such as bone or wood. Minerals precipitate out of solution and fill the pores and empty spaces. In the case of wood, petrification occurs when cellulose, hemicellulose, and lignin within the cell walls of the woody tissue act as a framework to preserve cell structure. Silicates, iron oxides, metal sulfides, native elements, carbonates, and sulfates can be involved in permineralization. Silicified wood is the most common and provides the most detailed preservation of cell structure.

The specimen above is a cross-section of a limb permineralized with silica. Volcanic material often serves as a source of silica for wood and bone. Volcanic activity resulting in pyroclastic flows, lahars, and ash falls can bury portions of forests that later become permineralized. Many permineralized specimens retain patterns of cell structure. Both cell structure and insect damage, in the form of galleries, have been preserved in the above specimen.

Silicified Fossil Wood Composition

When one holds a specimen of silicified wood it certainly appears to be made entirely of mineral matter with no original cellular material remaining. However, when examined under magnification many specimens reveal microscopic cellular structure leaving one to wonder if some of the original organic matter is still present. It is informative to make some basic comparisons between fresh wood and silicified fossil wood.

Cellulose, hemicellulose and lignin account for over 95% of the dry weight of wood (Leo & Barghoorn, 1976). The average density of 43 species of extant softwoods and 96 species of extant hardwoods examined by Hoadley is 0.53 g/cm^3 (Hoadley, 1990). The average density of the softwoods alone was 0.43 g/cm^3 , while for the hardwoods it was 0.57 g/cm^3 . Silicified wood generally contains more than 90%, by weight, of silica (Leo & Barghoorn, 1976; Sigleo, 1978; Furuno et al., 1986 II; Mustoe, 2008). Woods mineralized with opal have densities of 2.04 g/cm^3 or less. Woods permineralized with quartz have densities of 2.34 g/cm^3 or greater (Mustoe, 2008). Leo and Barghoorn (1976) note that many mineralized woods preferentially fracture toward a radially longitudinal plane as do non-mineralized woods. They hypothesized that this is due to retention of wood in the permineralized specimen or to discontinuities in silica deposition predetermined by the original wood structure at the time of petrification.

How much of the original wood is present? The first well documented attempt to answer this question was carried out by St. John (1927). St. John examined 25 prepared sections of various silicified wood specimens for cell structure under a light microscope. The sections were treated with a solution of one third hydrofluoric acid and two-thirds alcohol to remove silica and then reexamined under the microscope. Some specimens retained most or some of the structure indicating the presence of organic matter. Other specimens lost all of their structure with no trace of organic matter.

Mustoe (2008 and written personal communication, 2011) employed a more quantitative method to determine the presence of organic matter utilizing heat to destroy residual organic matter and measuring loss in mass. Mustoe concluded that most of the plant tissue is destroyed during silicification. Sigleo (1978) isolated lignin derivatives from 200 Ma *Araucarioxylon arizonicum* specimens demonstrating that small traces of relic organic matter can persist after many millions of years. Overall, evidence suggests that very little of the original organic matter remains in silicified wood.

How do we account for the visual appearance of cellular detail in silicified specimens that have little to no organic material? Leo and Barghoorn (1976) outline five ways in which cellular detail may be retained in silicified specimens:

1. The actual wood may remain intact after permineralization.
2. Products from the breakdown of cell walls may be immobilized in silica close to their site of origin.
3. Variations in the mineralogy of successive silica generations, including color, texture, and impurities.
4. Infiltration of foreign tar-like organic matter into the specimen.
5. Patterns of entrapped air, which darken silica.

Specimens from the same wood deposit can vary in how much structure is retained. Even single specimens may exhibit variation in the retention of wood structure. The idea that variations in mineralogy lead to differences in texture accords with my own experience. I have specimens from Sweet Home Oregon that exhibit beautiful annual rings. Upon closer inspection with a 10x loupe, variations in cellular detail are immediately apparent. In some areas that have a grainy texture, described by collectors as “sugary”, no cellular detail is revealed. In other areas, on the same specimen, the grain size of silica is so fine that wood histology can be studied with much satisfaction. Do these differences in how cell structure is preserved represent different taphonomic pathways or different stages within the same pathway? What are the conditions and processes that lead to the formation of siliceous petrifications?

Geochemical Conditions for Silicification

Silicified wood forms in principally two geologic environments. Trees transported by streams and rivers can become buried in the fine-grained fluvial sediments of deltas and floodplains or volcanic ash can bury trees while still upright (Mustoe, 2003). Fresh wood entombed in soft mud beneath water carrying large amounts of sediment may set up conditions necessary for fossilization. Rapid burial in volcanic ash is the initial stage for many fossil woods preserved with silica (Leo & Barghoorn, 1976). Volcanic ash acts as

an abundant source of silica for groundwater. The presence of water is important for several reasons: it reduces oxygen thereby inhibiting tissue deterioration from aerobic fungi, acts as an agent for the alteration of ash, maintains wood shape for maximum permeability, and creates a medium for the transport and deposition of silica.

The conditions of temperature and pressure during fossil wood formation are equivalent to those found in sedimentary environments of shallow depth. Excessive pressures would deform wood shape and tissues. Excessive temperatures (above 100⁰C) break down wood substances. The pH of the sediment-laden water within the wood is probably neutral to slightly acidic. Wood chemically breaks down at pH values below 4.5 and above 7. Silica is highly soluble at a pH of above 9 making precipitation less likely. The weathering of volcanic ash may produce a pH that is quite high (alkaline), which would release silica into solution making it available for emplacement in wood as the pH is lowered (Leo & Barghoorn, 1976). These physical and chemical parameters help to define the environmental conditions in which wood can act as a template for silica deposition.

A study of silicified wood from the Triassic-aged Chinle Formation of Arizona supports the parameters above. Sigleo (1979) compared the geochemistry of silicified wood and its associated sediments (sandstone with some siltstone and clay) to determine the environmental conditions for the process of wood mineralization. Fossil wood that has stayed in place since deposition and mineralization was carefully chosen for the study. The abundance of minerals and trace elements were measured from the core of the fossil wood to its periphery. Abundance of the same minerals and trace elements were measured in associated sediments and clays from the periphery of the specimen up to 3 meters away. The clay consisted of 80-90% montmorillonite, which formed from volcanic ash. Identical aluminum concentrations in the clay at the boundary of the fossil and within the periphery of the fossil wood suggest that montmorillonite co-precipitated with silica. The abundance of most trace elements increased from the core of the fossil to its periphery, with some notable exceptions.

Antimony (Sb) was found to be much more abundant within the fossil wood than in surrounding sediments with its highest concentrations at the core where carbon was also the most abundant. The abundance of uranium was highest in the carbonaceous core and decreased to the periphery of the fossil wood. Uranium and antimony are more mobile when in an oxidized state, but precipitate when reduced. In contrast, the abundance of manganese, which is more soluble in a reduced state, was low within the fossil specimen and had its highest concentration within the sediments adhering to the branch. Clays in the associated sediments were depleted of rare earth elements (REE) relative to the total sediments. REE can be leached from clays in soils with a pH of 4-5.

Sigleo (1979) concluded that the geochemistry of the fossil wood and associated sediments supports a fossil-forming environment that was anoxic and slightly acidic. The silicification process occurred at surface temperatures and pressures associated with typical surface and groundwater conditions. There was no evidence of alkaline conditions or exceptionally high silica concentrations in solution. A continuous supply of silica in solution was provided by the hydrolysis of volcanic ash. Later we will see evidence for secondary stages of silicification associated with hydrothermal events in Chemnitz fossil wood.

The Process of Wood Silicification

Leo and Barghoorn (1976) developed a hypothetical model for wood silicification based upon wood anatomy, a low temperature laboratory process for incipient silicification, and inferred geochemical parameters found in natural settings. Leo and Barghoorn hypothesized that there is a chemical affinity between wood and silica through hydrogen bonding. Several observations support the idea that relative unaltered wood may actually serve as a silica sink through hydrogen bonding. Coalified wood does not silicify well as it has lost functional groups capable of hydrogen bonding. Carbonate, sulfide, and fluoride petrifications are less common and of lower quality possibly because these ions do not establish hydrogen bonds as well as silica. Silicified woods are often encased within a matrix that is not cemented with silica, suggesting a differential affinity for silica between the wood and the surrounding sediment.

Leo and Barghoorn's experiments with artificial silicification of wood, described later, also support the idea that wood has an affinity for silica. According to their hypothesis, when wood is permeated by silica solution, hydrogen bonding links silicic acid to hydroxyl groups on cellulose making up the inner cell wall. As water is lost silicic acid is polymerized into opal. Layers of silica are deposited with the wood acting as a template. Initially, silica is fixed to the inner cell wall along the perimeter of the tracheid lumen and infill pits connecting adjacent tracheids. During initial stages of permineralization silica deposition fills voids, especially the lumina.

Cell walls may be replaced with silica in later stages of silicification. To replicate cell structure with high fidelity a balance between wood degradation and mineral deposition must be achieved. The amorphous silica that initially permeates wood is highly hygroscopic (attracts water) and is highly permeable to fluid flow. The rate at which this silica crystallizes to more impervious forms is extremely slow in geologic terms. Thus, long after silicification begins the influx of silica and the migration of degraded organic matter can continue through the porous medium.

As silicification proceeds to advanced stages cellulose degrades leaving more room for the emplacement of silica between cells and within cell wall layers. Lignin, under anaerobic conditions, is the most decay resistant compound in wood and continues to act as a template for structural detail. In fact, fossil woods show an increase in the ratio of lignin to holocellulose (cellulose & hemicellulose) when compared with contemporary counterparts. Specimens aged Eocene or older are devoid of holocellulose. Thus, lignin is the last organic matter to be replaced. The balance between removing organic matter and the deposition of minerals is often not complete so, some organic matter remains in many petrifications. As the process continues silica deposits in intercellular spaces and voids created by shrinkage wood degradation.

Silica that initially fixes to the wood structure is amorphous. This amorphous silica is unstable and slowly crystallizes to more stable forms. The transition to more stable forms of silica involves continued polymerization and water loss. Higher ordered forms of opal

are created through this process and eventually lead to the thermodynamically more stable silica quartz. Multiple studies have examined natural wood petrifications representing different fossil deposits providing insights into the physical and chemical processes involved in wood silicification. Many of these studies lend support for the work of Leo and Barghoorn.

Buurman (1972) examined fossil wood specimens preserved with a variety of minerals using X-ray diffraction, optical and scanning electron microscopy. We will summarize his findings relating to silicification. In one group of silicified woods Buurman found evidence suggesting that wood preservation is best when disordered tridymite (opal-CT) replaces cell walls or when this opal is subsequently transformed to chalcedony through recrystallization. In both instances, Buurman suggests the fossil wood has formed by replacement rather than filling. A second group of silicified woods preserved with chalcedony and quartz retained some woody tissue. Buurman suggested that these specimens had formed through permineralization (filling). Buurman concluded that replacement and permineralization are distinct processes.

In a more detailed study, Scurfield and Segnit (1984) examined 75 fossil wood specimens from Australia using X-ray diffraction, differential thermal analysis, electron probe techniques, optical and scanning electron microscopy. Their study found that replacement of the cell walls of tracheids and vessels occurred in addition to permineralization. They conclude that petrification of wood occurs in five stages, summarized as follows:

1. Wood is permeated by silica solution or colloid.
2. The pores of cell walls are penetrated.
3. Progressive dissolution of cell walls occurs as a mineral framework builds to maintain wood structure.
4. Silica deposits in voids, intercellular spaces, and finally cell lumina.
5. Lithification occurs, as water is lost. Silica may transform from one form to another by pseudomorphic replacement and/or repeated solution and recrystallization.

Scurfield and Segnit found evidence, in the specimens they studied, for transformation from opal-CT to chalcedony and chalcedony to quartz. Evidence for the conversion of opal-A to opal-CT was not strong. They also hypothesized that the rate of cell wall breakdown may determine whether opal-CT or chalcedony is the initial replicating substance.

Furuno et al. (1986 I & II) used light microscopy, SEM, electron probe X-ray microanalysis (EPMA), polarizing microscopy, and X-ray diffraction to study the anatomy and mineralization of Pliocene and Miocene silicified woods collected in Japan. Chemical and physical parameters such as color, hardness, reaction to hydrofluoric acid on fractured surfaces, and loss on ignition were also examined. Three samples representing the Pliocene were collected from the Mukaiyama Formation. Three samples representing the Miocene were collected from the Hata, Fujina, and Kori Formations.

Two *Sequoia* petrifications of Pliocene age are black in color. When fractured radially and treated with hydrofluoric acid these specimens produced silica casts of tracheid lumens. The cell walls of these specimens are not silicified and retain substantial organic matter. Cell lumens and pit chambers of these specimens are permineralized with opal-CT and some quartz, with one specimen showing more quartz than the other. By weight one specimen is 22.89% organic matter and 77.11% silica while the other is 20.56% organic matter and 79.44% silica. A third *Tsuga* petrification of Pliocene age is white to light brown in color. When fractured radially and treated with hydrofluoric acid isolated silicified tracheids were produced. The cell walls of this specimen are preserved in silica. The lumens and cell walls are preserved in opal-CT and some quartz. By weight the specimen is 2.42% organic matter and 97.68% silica.

One *Podocarpus* petrification of Miocene age is black in color. Cell lumens and cell walls are preserved in mostly quartz. The *Podocarpus* specimen contains some carbon in the cell walls and in resin cells. The authors hypothesize that resin within the resin cells may have fossilized into amber. By weight the *Podocarpus* specimen is composed of 5.93% organic matter and 94.08% silica. A second Miocene aged *Tsuga* specimen is light grey

in color. The Miocene-aged *Tsuga* has cell lumens and walls preserved in quartz. By weight this specimen is 0.09% organic compounds and 99.91% silica. One *Celtis* petrification, of Miocene age, is the only angiosperm dicot in the study and is light grey to brown in color. The *Celtis* specimen has cell lumens and cell walls preserved in quartz. By weight the *Celtis* specimen is 0.90% organic matter and 99.10% silica. Hydrofluoric acid applied to radially fractured surfaces on Miocene samples did not produce lithomorphs as easily as the Pliocene samples.

The samples in this study show a correlation between specimen color and its carbon content. The study also exhibits a correlation between the extent of silicification and time. Finally, there seems to be a pattern of increasing quartz content over time. Furuno et al. (1986 I & II) proposed the following phases for the silica mineralization of wood.

1. Deposition of silica filling in voids like cell lumens and pit chambers, but no penetration of silica into the walls, which remain.
2. Formation of casts of lumens by deposition of silica followed by loss of wall substance.
3. Deposition of silica in the voids and penetration of silica into the wall, some of which are replaced by silica.
4. Deposition of silica in the voids and penetration of silica into the walls, most or all of which are completely replaced, and in some cases loss of the intercellular substance.

The authors note that phase 2 was not observed in their study. Furuno et al. (1986 II) present the following scenario for wood silicification. First opal A dissolved in an alkaline solution that permeated wood. Silica precipitated within the acidic wood. Opal-CT was formed. The mineral was kept in a solid state and over tens of millions of years the opal-CT was crystallized to quartz. In the course of time all of the silica minerals were transformed to quartz.

Jefferson (1987) studied the preservation of Cretaceous-aged, silicified conifer wood from Alexander Island, Antarctica. Microscopic examination was made of acetate peels and thin sections made in transverse, tangential longitudinal, and radial longitudinal planes. Fractured surfaces, which broke preferentially in the radial plane, were examined using SEM. EDAX was utilized to identify the amount of silica and organic materials present in the cell walls as well as the distribution of minerals filling cell lumina.

Alexander wood in which silica infiltrated lumina without penetrating cell walls is poorly preserved. Cell walls in these specimens are reduced to thin lines of carbon inclusions embedded in silica. Well-preserved Alexander wood resulted from a process in which silica infiltrated cell lumina and impregnated cell walls. Cell walls in well-preserved specimens contain between 82 and 87% silica with only scattered carbonized residue remaining. Jefferson surveys how the preservation and form of bordered pits along fractured longitudinal surfaces can be used to determine the extent to which silica infiltrated pit chambers. For example silica infilling creates casts of pit chambers.

Silicified microfibrils making up the cell walls of Alexander wood are 20 to 150 times larger in diameter than extant conifers. Tracheids of Alexander wood often contain preserved fungi hyphae and lensoid-ovoid organic bodies interpreted as fungal spores. The author suggests that cell walls of Alexander wood were delignified by fungal activity separating microfibrils, making them available for silica coating. Growth of silica on fibrillar bundles exposed by fungal activity allowed cell wall structures to be preserved. Thus, cell walls were not replaced; rather, they were preserved through a process of silica infiltration and impregnation enhanced by biogenic degradation.

Euhedral, cubic iron sulfide crystals enclosed in silica are found within the lumina of some tracheids. The growth of pyrite crystals indicates an initial reducing environment. Quartz crystals within cell lumina most often grow inward without penetrating cell walls. In some lumina apatite and colophonite fill up the remaining space not occupied by quartz. Thus, it appears that the cell walls were already silicified when cell lumina were mineralized. Furthermore, the presence of apatite and colophonite probably represent a

major change in the composition of the permineralizing solution. Jefferson proposed a two-phase silicification process for Alexander petrifications.

1. Silica impregnated cell walls. Biogenic delignification and decay of the cell wall opened up spaces and isolated microfibrils creating interfibrillar porosity. Silicic acid precipitated and polymerized onto the microfibrils, and filled the interfibrillar porosity. The amorphous silica coating microfibrils crystallized into chalcedony and microcrystalline quartz. The author references work that states the subsequent transformation and ordering of silica would be expected to take millions of years.
2. Cell lumina were infilled by chalcedony and euhedral-subhedral quartz crystals and or apatite and cellophane.

Jefferson concluded that Alexander wood supports the two-stage theory of wood silicification proposed by Leo and Barghoorn (1976). However results from the study of Alexander wood suggest that the impregnation of cell walls can be promoted by biogenic degradation.

The progressive transformation of opal-A to opal-CT to chalcedony and finally quartz is an important aspect of the accepted model for wood silicification. Recent work by Mustoe (2008) reveals that the silica transformation aspect of this model is inconsistent with the mineralogy of fossil wood in the Florissant Formation. Mustoe examined 15 specimens representing six silicified stumps. The samples were analyzed using X-ray diffraction, X-ray fluorescence, scanning electron microscopy/energy-dispersive X-ray spectrometry (SEM/EDX), and optical microscopy. Basic physical properties including density, color, and loss on ignition were also determined.

Some of the specimens were permineralized with only opal-CT, others were a combination of opal-CT and chalcedony, and still others were quartz. In specimens permineralized with both opal-CT and chalcedony the two silica phases appeared to coexist as primary minerals. Thus, evidence for the transformation of opal-CT to

chalcedony was missing. Evidence gathered by this study suggests that the Florissant specimens were directly mineralized with chalcedony. The precipitation of opal, chalcedony, and quartz are influenced by concentrations of dissolved silica. Opal is precipitated with high concentrations of dissolved silica while chalcedony is precipitated with low concentrations and quartz still lower. Mustoe speculates that these geochemical characteristics may explain the patterns of mineralization found at Florissant. Mustoe concluded that petrification at Florissant occurred in several stages.

1. First, amorphous silica precipitated on cell wall surfaces.
2. Second, opal-CT and chalcedony filled cell lumina.
3. Finally, chalcedony filled fractures that crosscut permineralized tissues in some specimens.

Spaces between adjacent tracheids were often unmineralized, making the fossil wood permeable to water and susceptible to cleaving radially, tangentially and transversely from freeze-thaw weathering. This finding has important implications for the preservation of specimens at Florissant Fossil Beds National Monument. Mustoe's findings are important because they suggest that petrification may occur through multiple processes or pathways.

Witke et al. (2001) used Raman and cathodoluminescence spectroscopy to study the chemical composition and structural order of silicified plants from the 290 million year old Chemnitz Petrified Forest. Samples of the seed fern *Medullosa*, gymnosperm *Dadoxylon*, sphenopsid *Calamodendron striatum*, and tree fern *Psaronius* were used in the study. Tracheid and sclerenchyma cells making up vascular tissues are preferentially preserved in Chemnitz fossil plants. Cell walls are preserved primarily in microcrystalline α -quartz. In areas where tissue is not preserved as in the pith of *Medullosa* one finds banded agate structures composed of phanocrystalline and microcrystalline α -quartz along with moganite. A very low percentage of original organic material remains in the Chemnitz silicified plants. Raman spectra of carbonized material dispersed within Chemnitz petrifications reveals a rank equal to bituminous and

anthracite coals. Witke et al. (2001) proposed the following steps for the mineralizations of Chemnitz petrifications.

1. First, plants were mineralized with quartz and fluorite.
2. Second, a hydrothermal alteration transformed the silica. Iron oxides were associated with this process. Minor residues of carbonaceous material of anthracite rank found in Chemnitz specimens seem to be consistent with a hydrothermal event.
3. The third step consisted of secondary mineralizations with calcite and barite in cracks of the former wood.

Dietrich et al. (2013) used backscatter electron imaging (BSE) and electron backscatter diffraction (EBSD) in a scanning electron microscope to study the ordering of silica preserving xylem tissue in three different fossil tree forms found in Chemnitz Petrified Forest.

The study of Chemnitz petrifications included the root mantle of the tree fern *Psaronius*, vascular segments in the pith of the seed fern *Medullosa stellata*, and the secondary xylem of the gymnosperm *Dadoxylon*. Former open spaces and specific tissue structures were found to be correlated with different silica ordering.

Tracheid cell walls in the aerial roots of *Psaronius* are largely preserved by well-ordered microcrystalline quartz grains. The thickened cell walls of the sclerenchyma fibers, making up the outer boundary of the aerial root, are preserved with extremely fine-grained but well-ordered quartz. Cell lumina are filled with cryptocrystalline quartz. Tracheid cell walls in *M. stellata* exhibited multiple microcrystalline layers outlining the former cell wall layers. In fact crystal growth directions within these layers seem to mirror former cellulose fibril orientations. As in the *Psaronius*, cell lumina were largely filled with cryptocrystalline quartz. Tracheid cell walls in the secondary xylem of *Dadoxylon* are preserved with microcrystalline quartz. Cell lumina are filled mostly with

cryptocrystalline quartz or more infrequently with microcrystalline quartz or large fluor spar crystals.

In general the cell lumina of all three specimens are filled with cryptocrystalline quartz, while the cell walls were preserved with microcrystalline quartz. Microcrystalline quartz grain size decreased with tracheid cell diameter. *Psaronius* tracheid cell walls are preserved with the largest grain size, while the cell walls of *Psaronius* sclerenchyma, *M. stellata* tracheids, and *Dadoxylon* tracheids are preserved with a finer grain size. The tissues of these plants vary in their proportions of cellulose, hemicellulose, and lignin. The results of this study suggest that tissue composition affects silicification ordering in petrifications. Dietrich et al. (2013) proposed the following stages of petrification to explain the patterns of silica ordering observed in the tissues of Chemnitz specimens.

1. Silica solution permeates the porous xylem tissue and forms a silica gel inside the tracheid lumina starting at the inner cell walls.
2. Thus cell lumina are quickly preserved in silica, which may be transformed later to cryptocrystalline silica or to α -quartz.
3. The gel cast of the lumina is initially porous and allows a continued influx of silica solution (presumably in a hydrothermal process), which over longer periods of time permeates into the ligno-cellulose making up the former cell walls and intercalates the cellulose fibrils.
4. Cellulose fibrils act as templates for microcrystalline growth of silica. Thus, the preserved cell walls can be distinguished from the cell lumina by different crystal growth.
5. In the third stage, agate and/or larger grains of microcrystalline quartz form in areas with fewer precipitation sites such as cell corners, central piths and fissures resulting from cracking, drying, and tissue degradation.

Is there a place we can go to examine the silicification of wood occurring in more recent times? Karowe and Jefferson (1987) investigated the initial stages of silicification by examining trees buried by Mount St. Helens lahars or mudflows dated at 1980, 1885,

A.D. 1450-1550 and 36,000 years B.P. Wood samples were examined using scanning electron microscopy and energy dispersive X-ray analyses. Wood buried in 1980 showed no significant mineral deposition. Wood buried in 1880 and A.D. 1450-1550 exhibited traces of silica on cell walls as well as cell wall decay. Wood buried 36,000 years B.P. showed silica impregnation of cell walls. Decay in these older specimens affected the secondary wall and removed the middle lamella. Karowe and Jefferson concluded that the increase in silica deposition as well as decay associated with the age of these trees supported the model of silicification proposed by Leo and Barghoorn in 1976.

The apparent increase in silica deposition was an exciting find. However, researchers at the University of Bonn were unable to reproduce the results of Karowe and Jefferson even when using specimens prepared from the same trees (Hellawell et al., 2011). Perhaps Karowe and Jefferson were looking at an instrumental artifact. Scientists at the University of Bonn are currently working on a paper that will explore the results of their study in more depth. It is clear that many petrified wood deposits, such as those found at Yellowstone, are associated with volcanic mudflows. George Mustoe has examined many Holocene wood specimens from mudflows and has found no evidence of silicification (Mustoe, written personal communication, 2012).

Time and Silicified Wood

Fossil plant deposits including petrified forests from around the world allow paleontologists to trace the evolutionary history of vascular plants from 420 Ma ago (Silurian) to the present (Kerp, 2002). Petrified forests throughout the world capture the public's imagination (Ransom, 1955; Dernbach, 1996; Dernbach and Tidwell, 2002; Daniels and Dayvault, 2006). Many want to know how long it takes to form natural petrified wood. Some Pleistocene deposits contain peat and wood fragments that can be carbon dated. Ice Age gravels deposited 12,000 years ago contain fresh looking wood pieces. Wood dated at 15 million years weathering out of the Wilkes Formation in Washington can be carved with a pocketknife and ignited with a match (Mustoe, 2001). It is clear that wood can be preserved for long periods of time under the right conditions.

It is equally clear that wood can be quickly mineralized under the right conditions. Timbers in copper mines from Cyprus and Arizona have been found that contain copper (Daniels & Dayvault, 2006). Wood buried in ash produced from the 1886 eruption of Mt. Tarawera in New Zealand is mineralized with silica. Wood specimens recently exposed to hot springs in Yellowstone exhibit the beginning stages of silicification; however, geologic evidence suggests siliceous thermal springs have not been major sites of wood petrification (Leo & Barghoorn, 1976). Silicified wood from Wyoming contained enough organic material to be carbon dated at less than 3,000 B.P. X-ray diffraction reveals that these recently silicified woods are impregnated with amorphous opal (Leo & Barghoorn, 1976; Stein, 1982).

The question of how long it takes to form petrified wood also depends on the physical qualities of the fossil wood we have in mind. Are we looking at wood that is mostly intact and has cell lumina and intercellular spaces impregnated with minerals or fossil wood that has little to no wood remaining and has cellular detail replicated in opal-CT, chalcedony, and microgranular quartz? If we have in mind the latter then these recent petrifications are not what collectors think of as gem quality petrified wood, which can be cut and polished at the lapidary.

The initial emplacement of silica as a film may occur rapidly. Artificial silicification of wood in the lab and studies of natural silicified wood demonstrate that the physical state of silica in newly formed petrifications is amorphous (Leo & Barghoorn, 1976). Conversion of this silica to increasingly stable forms of opal-A (amorphous), to opal-CT (cristobaite & tridymite), to chalcedony (cryptocrystalline quartz), and finally to microgranular quartz requires millions of years (Leo & Barghoorn, 1976; Stein, 1982; Kuczumow et al., 1999). Under normal conditions conversion of opal to quartz requires tens of millions of years; however, under geothermal conditions the same process may occur in 50,000 years or less (Mustoe, 2003).

X-ray diffraction patterns for different aged silicified specimens examined by Stein support the well-established transformational sequence of opal-A to opal-CT, to quartz. A

Yellowstone Wyoming sample carbon dated at 2,430 years was composed of opal-A. A Pliocene-aged sample from the Sante Fe Formation of New Mexico was composed of opal-CT. A Miocene-aged sample from the Bozeman Lake Beds was composed of opal-CT and some quartz. A Late Eocene sample from Florissant, Colorado was composed of quartz. However, Mustoe (2008) has shown that some Florissant wood is permineralized with opal-CT and chalcedony as well. Still, chalcedony and microgranular quartz are the most common forms of silica found in fossil woods that are Eocene or older. X-ray diffraction studies, specific gravity measurements and indices of refraction all support an increase in silica ordering with increase in age (Stein, 1982).

Instant Petrified Wood?

Fascination with natural permineralized specimens has spurred interest in creating methods for artificial petrification. Artificial petrification reflects both scientific and commercial interests. Methods for artificial petrification have been devised as a way to study wood structure and model the initial stages of natural silicification. Artificial petrification is also used to develop wood composites and ceramics. Leo and Barghoorn (1976) document early attempts at creating artificial silicified woods in the 1500's by Basil Valentine and Johannes Kentmann. Experimental replication of these early recipes has not been successful. More recent attempts have produced some positive results.

Ryan W. Drum from the University of Massachusetts, Amherst describes his attempt at the laboratory silicification of twigs in a 1968 article that appeared in the journal *Science*. Twigs were soaked in solutions of sodium metasilicate, washed, and then treated with chromic acid to remove organic remains. Entire twigs did not remain intact; however, single cells and small aggregates of cells were replicated in silica. Drum described these replicas as very fragile and included electron micrographs of his results. Drum goes on to say that his in vitro silicification process might provide a method to study cellular spaces in 3-D, intercellular connections, and the morphology of woody cells.

Leo and Barghoorn (1976) improved upon Drum's experiments. Their procedure included boiling wood to degas and waterlog specimens. The wood was alternately

soaked in solutions of water and ethyl silicate at neutral pH and 70⁰C. Ethyl silicate decomposes to monomolecular silicic acid, which is thought to be the silicifying agent in natural processes. Nitric acid and potassium chlorate were used to remove organic matter. The silica lithomorphs that remained replicated cell structure and were more substantial than those produced from Drum's procedure. The silica lithomorphs were fragile and composed of amorphous silica. These silica lithomorphs resemble the first stages of permineralization observed in recently silicified specimens.

Persson et al. (2004) evaluated the use of sol-gel mineralization to study the wood morphology of spruce and birch xylem. Wood chips of birch, *Betula verrucosa*, and spruce, *Picea abies*, along with the pulp of spruce were used in the study. Spruce pulp was prepared using the Kraft process. The Kraft process uses a mixture of sodium hydroxide and sodium sulfide along with cooking at high temperatures (170⁰C) to degrade lignin and hemicellulose, converting the wood to a pulp consisting of almost pure cellulose fibers.

Wood chip samples and the pulp were soaked in ethanol and vacuum dried two times to facilitate impregnation. The prepared wood and pulp samples were immersed in a sol-gel mixture (polysilicic acid) for three days at 60⁰C. Silica casts of the wood and pulp were recovered by removing all organic material by heating to 575⁰C for 6 hours. The brittle silica cast replicas were studied using environmental scanning electron microscopy (ESEM) and transmission electron microscopy (TEM). Persson et al. (2004) found that their sol-gel casting medium penetrated and condensed on the ultrastructure of cell walls. The high-resolution silica casts were used to observe the three dimensional structure of xylem and pit structures connecting wood cells.

Experiments in artificial silicification described above have been used as methods to replicate the process of natural incipient silicification and to study the ultrastructure of wood. These experiments suggest that the organic cell structure of wood acts as a template for initial silica deposition. The fact that wood is removed in making silica-cast

replicas limits the use of these procedures for studying advanced stages of natural silicification.

More recently, Ballhaus et al. (2012) designed closed-system experiments at 100⁰C to simulate the silicification of trees buried by volcanic pyroclastics. Silica rich solutions were prepared by reacting powdered obsidian with water at 100⁰C for several days. Under these conditions it was found that silica and alkali oxides readily go into solution while aluminum oxide remains in the residue. The pH of the solution increases to values of 9.4-10.5. Wooden cubes made of Douglas-fir (*Pseudotsuga menziesii*) were reacted with the silica solution in an autoclave for up to 300 hours. In the presence of the wood the pH and silica concentrations decreased, while alkalis remained in solution.

Silica rich solutions were again prepared by reacting powdered obsidian with water at 100⁰C for several days. The solution was doped with NaOH to increase the pH values to 12.5 and 13.2 in order to increase the solutions silica concentration. Douglas-fir wood cubes were reacted with the solutions in autoclaves for 112 days. Periodically, slices of wood were prepared and analyzed for precipitates. After several days many of the cell lumina were infilled with silica. Most precipitates were found on wood that exhibited final pH values near neutral. Under SEM the silica precipitates appeared as microspheres of opal.

These experiments simulate and provide evidence in support of processes thought to be involved in the incipient permineralization of wood. Volcanic material rich in siliceous glass can be quite alkaline. When these solutions come into contact with wood the pH is lowered and silica becomes less soluble, precipitating onto wood surfaces. This pH gradient between the silica rich alkaline water and the acidic environment of the wood tissue acts as force to precipitate opal onto wood surfaces. A second force driving permineralization is the ability of wood tissue to extract silica out of solution. The decrease in the silica concentration in the presence of Douglas-fir wood cubes is indirect evidence that is consistent with Leo and Barghoorn's (1976) hypothesis that silica species chemically bond with hydroxyl groups on wood surfaces.

Ballhaus et al., (2012) used simple diffusion and advection models to estimate how long it would take to permineralize a tree with opal. Using Frick's Law a theoretical conifer tree trunk with a diameter of 100 cm and a length of 100 cm buried horizontally in a pyroclastic deposit would be permineralized through diffusion within an estimated time of 47,000 years. Using an advection model the same tree buried upright (*in situ*) would require approximately 3,600 years for cell lumina and intercellular spaces to become impregnated with opal. This estimate assumes wood structure remains intact. The results of this study are consistent with other findings and indicate that the incipient permineralization of large trees with opal is on a time scale of thousands of years.

The process of natural permineralization has also inspired the pursuit of artificial wood composites. These wood composites use fresh wood as a framework for creating either a wood composite or a ceramic. An October 1992 *Popular Science* news article read 'Instant petrified wood?' In reality researchers at the Advanced Ceramic Materials Lab at the University of Washington in Seattle were making wood ceramic composites. Wood is soaked in solutions of silica and aluminum and then oven-cured to create the composites. The solution penetrates the wood to a depth of up to 0.2 inches. The wood is abrasive, but can be worked with carbide tools. The authors speculate that these composites could be made with the same rock-hardness of petrified wood. The composite is wood impregnated with silica and aluminum up to a depth of 0.2 inches.

Yongsoon Shin and colleagues (Shin et al., 2001) at the Pacific Northwest National Laboratory (PNNL) developed a method for creating a silica-based ceramic that mimics wood structure. The process uses surfactants and silicate solutions to mineralize wood that has been soaked in an acid solution. After the silicate solution penetrates cell wall structures it is heated to high temperatures in air to oxidize the silicate and remove organic residue. This method creates a ceramic, which faithfully reproduces cellular structures in great detail as confirmed by SEM images. Shin et al. (2001) points out that, "Another important phenomenon related to the current study is natural petrification, which takes place over a very long period of time. In some cases the cellular tissue is completely replaced by silicate and other minerals. Our study not only points to a more

rapid approach to transforming organic tissues into ceramic materials, it may also shed some light on how natural petrification takes place (p. 731).”

An article on ChemicalProcessing.com entitled ‘Petrified wood yields super ceramics’ describes a process developed at PNNL for using wood to form the ceramics silicon carbide (SiC) and titanium carbide (TiC). The process involves soaking the wood in acid, infusing it with titanium or silicon, and baking it in an argon-filled furnace at 1,400⁰C. This process is the same as Shin’s 2001 study except for heating in an argon atmosphere instead of air. The 2001 and 2005 experiments used small blocks of pine and poplar wood. Both the macro and microstructure of the wood is preserved in this ceramic. The material has the strength of steel, and can resist temperatures of up to 1,400⁰C. PNNL scientist Yongsoon Shin is quoted as saying that one-gram of this material flattened has enough porosity to cover an entire football field. SEM and TEM images were used to study the microscopic structure of these ceramics (Shin et al., 2005). The SiC ceramics could be used for making filters, catalysts, cutting tools, abrasives, and coatings. The purpose of Shin’s research is to develop methods for using natural biological materials as templates to construct inorganic materials.

Hamilton Hicks was issued US patent 4612050 on September 16, 1986 for a mineralized sodium silicate solution used to create wood with the “non-burning characteristics of petrified wood” (Patent Storm). In one experiment a horse stall was set on fire with combustible materials. The treated wood showed signs of charring, but did not burn. The patent indicates that the treated wood is non-toxic and has an inherently bad taste. This bad taste prevents horses from “chewing or nibbling the wood to shreds”. The inventor speculates, “petrification” of the treated wood is achieved when minerals in his solution “replace the cells” and the solution hardens the wood. It would be interesting to compare the amount of wood still present as well as the nature and extent of silicification in this product with that found in naturally silicified wood.

Products referred to as “instant petrified wood” may provide insights into the initial stages of permineralization. However, many of the materials and procedures used to

make these products are not found in nature. Furthermore, procedures to make silica-cast replicas and ceramics remove wood after the initial permeation with artificial mediums. Products made from the initial emplacement of silica, represented by both artificial and recent natural petrifications do not resemble what a collector regards as gem quality petrified wood. Multiple lines of evidence suggest that natural fossil wood silicified with opal-CT, chalcedony and microgranular quartz requires millions of years to form.

Conclusion

Evidence for pathways that lead to the formation of silicified wood comes from studies of fossil wood from different aged deposits, laboratory procedures for artificial petrification, and examination of trees buried recently by volcanic deposits. The formation of silicified wood includes permineralization, replacement and recrystallization. A summary of an accepted model for natural silicification is as follows.

When wood is permeated by silica solution, hydrogen bonding links silicic acid to cellulose making up the inner cell walls. Silicic acid is polymerized into opal through water loss. Silica that initially fixes to the wood structure is amorphous and can recrystallize to a more stable form. Layers of silica are deposited with the wood acting as a template. Initially, silica is fixed to the inner cell walls and infills the lumina of tracheary elements (vessel elements and or tracheids) and the pits connecting adjacent tracheary elements.

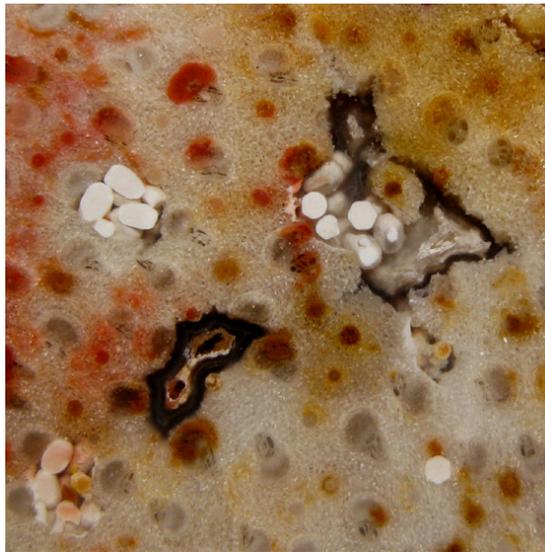
Cell walls may be replaced with silica as permineralization continues. To replicate cell structure with high fidelity a balance between the chemical and biological decomposition of wood and the precipitation of silica must be achieved. As silicification proceeds to more advanced stages cellulose degrades leaving more room for the emplacement of silica between cells and within cell wall layers. This replacement is not molecule-by-molecule. Lignin is the most decay resistant compound in wood and continues to act as a template for structural detail. Later, cracks and fractures are preserved with silica. A traditional model of silicification includes a transformation of the initial silica to increasingly more stable forms from opal-A to opal-CT to chalcedony and finally to

quartz. However, evidence for silica recrystallization is lacking in some specimens suggesting more than one pathway for silicified wood formation (Mustoe, 2008).

Studies of silicified wood from Florissant and Chemnitz demonstrate that cell walls and lumina can be preserved in different forms of silica. Thus, forms of silica that serve as the initial replicating material for cell walls and open spaces may be different from what initially permineralized the wood. Factors that affect what form of silica serves as the initial replicating material will lead to a better understanding of natural silicification pathways. One of these factors may include the plant tissues themselves. Examination of microstructure in petrifications of Chemnitz encourages further investigations into how tissue composition affects what form of silica may act as a replicating material (Dietrich et al. 2013).

Acknowledgments

I would like to thank George Mustoe, Dagmar Dietrich, Yongsoon Shin, and Jim Mills for their expertise and encouragement.



Termite Coprolites in Permineralized *Palmoxylon* Fiber
Oligocene; Catahoula Formation
Rapides Parish, Louisiana

Bibliography

- Ballhaus, C., Gee, C.T., Bockrath, C., Greef, K., Mansfeldt, T, and Rhede D. (2012). The silicification of trees in volcanic ash-An experimental study. *Geochimica et Cosmochimica Acta* 84: 62-74.
- Buurman, P. (1972). Mineralization of Fossil Wood. *Scripta Geologica*, vol. 12, pp. 1-43.
- ChemicalProcessing.com. Petrified wood yields super ceramics, <http://www.chemicalprocessing.com/articles/2005/512.html>
- Daniels, F.J. and Dayvault, R.D. (2006). *Ancient Forests: A Closer Look at Fossil Wood*. Western Colorado Publishing Company: Canada.
- Dernbach, U. (1996). *Petrified Forests: The World's 31 Most Beautiful Petrified Forests*. Germany: D'ORO.
- Dernbach, U. & Tidwell, W.D. (2002). *Secrets of Petrified Plants: Fascination from Millions of Years*. Germany: D'ORO.
- Dietrich, D., Lampke, T., & Rossler, R. (2013). A microstructure study on silicified wood from the Permian Petrified Forest of Chemnitz. *Palaontologische Zeitschrift: Scientific Contributions to Palaeontology*. Berlin Heidelberg: Springer-Verlag. DOI 10.1007/s12542-012-0162-0.
- Drum R.W. (1968). Silification of Betula Woody Tissue in vitro. *Science*, 161, pp. 175-176.
- Furuno T., Watanabe T., Suzuki N., Goto, T., and Yokoyama, K. (1986). Microstructure and Silica Mineralization in the Formation of Silicified Woods I. Species identification of silicified woods and observations with a scanning electron microscope. *Journal of the Japan Wood Research Society*. Vol 32, No 6, pp. 387-400. Japan: Mokuzai Gakkaishi.
- Furuno T., Watanabe T., Suzuki N., Goto, T., and Yokoyama, K. (1986). Microstructure and Silica Mineralization in the Formation of Silicified Woods II. Distribution of organic carbon and the formation of quartz in the structure of silicified woods. *Journal of the Japan Wood Research Society*. Vol 32, No 8, pp. 575-583. Japan: Mokuzai Gakkaishi.
- Hellawell, J., Gee, C. T., Ballhaus, C., Clynne, M. A. and Sander, P. M. (2011). *Silicification of wood: identifying ancient and present-day processes*. Abstract for poster presentation, The Palaeontological Association 55th Annual Meeting, Plymouth University, UK.
- Hoadley, R.B. (1990). *Identifying Wood: Accurate Results with Simple Tools*. The Taunton Press: Newtown, Connecticut.

Jefferson, T.H. (1987). The Preservation of Conifer Wood: Examples from the Lower Cretaceous of Antarctica. *Palaeontology*, vol 30, part 2, pp. 233-249.

Karowe, A.L. & Jefferson, T.H. (1987). Burial of Trees by Eruptions of Mount St. Helens, Washington: Implications for the Interpretation of Fossil Forests. *Geological Magazine*, vol 124, no. 3, pp. 191-302.

Kerp, H. (2002). The Rhynie Chert: The Oldest and Most Completely Preserved Terrestrial Ecosystem. In Dernbach, U. & Tidwell, W.D. *Secrets of Petrified Plants: Fascination from Millions of Years* (pp. 23-27). D'ORO: Germany.

Kuczumow A., Vekemans, B., Schalm, O., Dorrine, W., Chevallier, P., Dillmann, P., Ro, Chul-Un, Janssens, K., & Van Grieken, R. (1998). Analysis of petrified wood by electron, X-ray and optical microprobes. *Journal of Analytical Atomic Spectrometry*, vol 14, pp. 435-446.

Leo, R.F. & Barghoorn, E.S. (1976). Silicification of Wood. *Botanical Museum Leaflets, Harvard University*, vol. 25, no 1.

McCafferty, P. (1992). Instant petrified wood? *Popular Science*, Oct, pp. 56-57.

Mustoe, G.E. (2001). Washington's Fossil Forests. *Washington Geology*, vol 29, no1/2, pp. 10-20.

Mustoe, G.E. (2003). Microscopy of Silicified Wood. *Microscopy Today*, vol 11, no 6, pp. 34-37.

Mustoe, G.E. (2008). Mineralogy and geochemistry of late Eocene silicified wood from Florissant Fossil Beds National Monument, Colorado, in Meyer, H.W., and Smith, D.M., [Eds.], *Paleontology of the Upper Eocene Florissant Formation, Colorado* (pp. 127-140). Geological Society of America Special Paper 435.

Mustoe, G.E., *Written Communication*, March 2011.

Mustoe, G.E. *Written Communication*, November 2012.

Patent Storm. US Patent 4612050 - Sodium silicate composition, <http://www.patentstorm.us/patents/4612050/fulltext.html>

Ranson, J.E. (1955). *Petrified Forest Trails: Guide to the Petrified Forests of America*. Oregon: Mineralogist Publishing Company.

Persson, P.V., Fogden, A., Hafren, J. Daniel, G. & Iversen, T. (2004). Silica-Cast Replicas for Morphology Studies on Spruce and Birch Xylem. *IAWA Journal*. Vol 25, pp. 155-164.

Scurfield, G. & Segnit, E.R. (1984). Petrification of Wood by Silica Minerals. *Sedimentary Geology*, 39, 149-167.

Shin, Y., Liu J., Chang J.H., Nie Z., & Exarhos, G.J. (2001). Hierarchically Ordered Ceramics Through Surfactant-Templated Sol-Gel Mineralization of Biological Cellular Structures. *Advanced Materials*, 13, pp. 728-731.

Shin, Y., Wang, C., & Exarhos, G.J. (2005). Synthesis of SiC Ceramics by the Carbothermal Reduction of Mineralized Wood with Silica. *Advanced Materials*, 17, pp. 73-76.

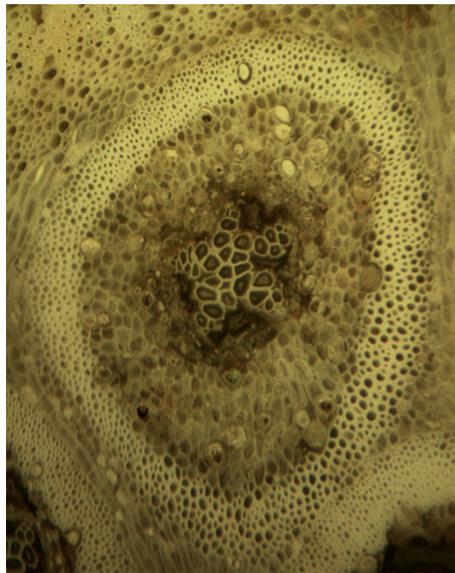
Sigleo, A.C. (1978). Organic Geochemistry of Silicified Wood, Petrified Forest National Park, Arizona. *Geochimica et Cosmochimica Acta*, vol 42, pp. 1397-1405.

Sigleo, A.C. (1979). Geochemistry of Silicified Wood and Associated Sediments, Petrified Forest National Park, Arizona. *Chemical Geology*, 26, pp. 151-163.

St. John, R.N. (1927). Replacement vs. Impregnation in Petrified Wood. *Economic Geology*, vol 22, pp. 729-739.

Stein, C.L. (1982). Silica Recrystallization in Petrified Wood. *Journal of Sedimentary Petrology*, vol 52, no 4. pp. 1277-1282.

Witke, K., Gotze, J., Rossler, R. Dietrich, D. Marx, G. (2004). Raman cathodoluminescence spectroscopic investigations on Permian fossil wood from Chemnitz—a contribution to the study of the permineralisation process. *Spectrochimica Acta Part A*, 60, pp. 2903-2912.



Titea singularis Aerial Root
Bieland, Maranhao Province, Brazil
Pedra de Fogo Formation Permian